

**Effect of Ligand Coordination on Complex Formation:
Synthesis & Structural Studies of metal(I) salts
containing the $\text{N}(\text{SO}_2\text{CF}_3)_2$ and OTeF_5 groups**



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| 14. ABSTRACT The šcisoidŠ form is less common. In the CCDC, only 6 structures show this conformation where as the štransiodŠ form occurs in 15 remaining structures The šcisoidŠ conformation results from stronger cation-anion interaction The šcisoidŠ exclusively when anion is chelated to the metal center The štransoidŠ form dominates in structures containing a šfreeŠ anion NO structure known with both šcisoidŠ AND štransoidŠ geometry | | | | | |
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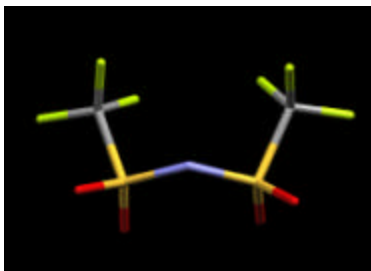
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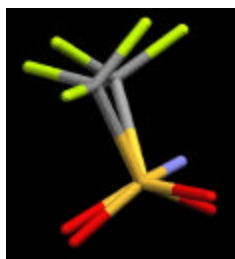
Department of Chemistry, University of California, Riverside CA 92521



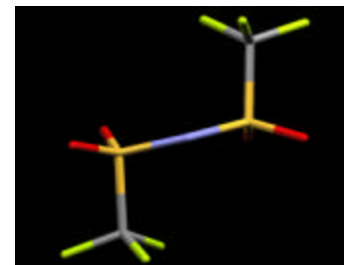
Coordination & isomerism in $N(\text{SO}_2\text{CF}_3)_2$



“Cisoid”



**C-S--S-C
“torsion”**



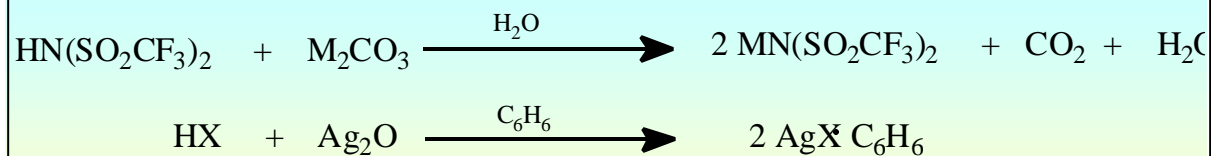
“Transoid”

- ✓ The “cisoid” form is less common. In the CCDC, only 6 structures show this conformation where as the “transoid” form occurs in 15 remaining structures
- ✓ The “cisoid” conformation results from stronger cation-anion interaction
- ✓ The “cisoid” exclusively when anion is chelated to the metal center
- ✓ The “transoid” form dominates in structures containing a “free” anion
- ✓ NO structure known with both “cisoid” AND “transoid” geometry

DesMarteau, Pennington *et al.*, Solid State Sciences, 2002, 4, 1535-1545



Synthesis of metal(I) derivatives



These salts are colorless crystalline materials. Some turn amorphous with time

$\nu_{\text{Te-O}}$ (cm^{-1}): IR (Ra) at ~865 (860)

$\nu_{\text{as SO}_2}$ (cm^{-1}): IR (Ra) at
~1320(~1328)

^1H NMR: C_6H_6 peak at 7.6-7.7 ppm

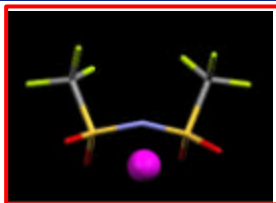
Uncoordinated benzene: 7.3

^{19}F NMR: ~-78 ppm (CF_3)

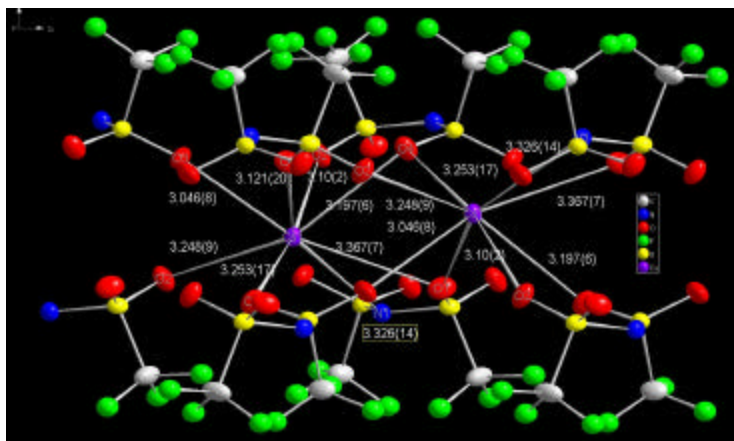
- ✓ **These salts are colorless and crystalline.**
- ✓ **Recrystallization from iso-propylalcohol gave anhydrous salts.**
- ✓ **Some of these salts turn amorphous with time**



Structure of $\text{CsN}(\text{SO}_2\text{CF}_3)_2$ salts



$\text{CsN}(\text{SO}_2\text{CF}_3)_2$

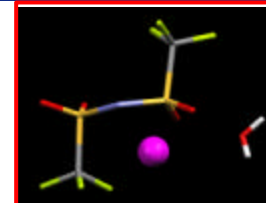


Monoclinic $C2/c$ [$\beta = 91.92(1)^\circ$]

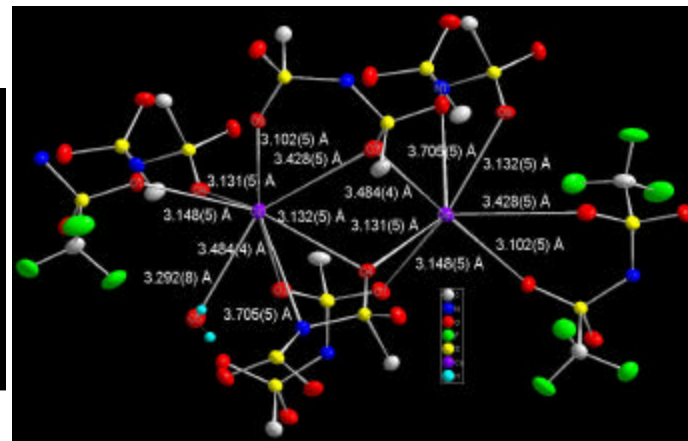
$a = 22.509(12)$, $b = 7.029(4)$, $c = 13.519(7)$ [Å]

Volume (Å³) = 2137.5(19), $Z = 8$, $T = 298$ K

$R1 = 0.0399$, $S = 1.024$



$\text{CsN}(\text{SO}_2\text{CF}_3)_2 \cdot \text{H}_2\text{O}$



Tetragonal $I-4$

$a = 16.903(1)$, $c = 7.8933(6)$ [Å]

Volume (Å³) = 2255.2(3), $Z = 6$, $T = 298$ K

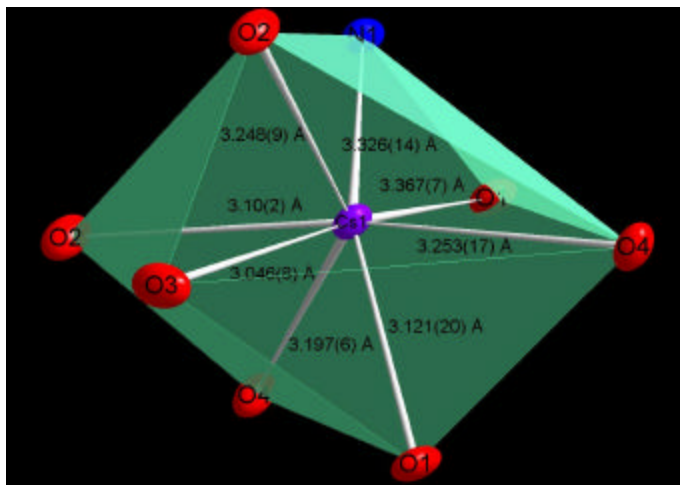
$R1 = 0.0307$, $S = 1.20$



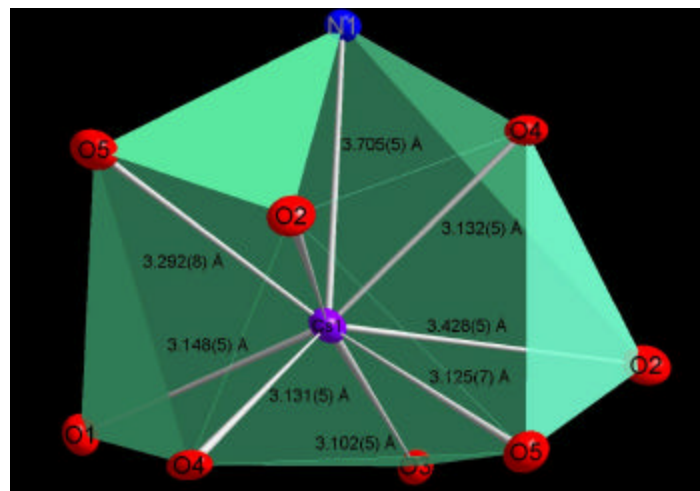
Coordination environment of Cs in $\text{CsN}(\text{SO}_2\text{CF}_3)_2$ salts



Octa-coordinated with a short Cs-N bond



Nona-coordinated with a long Cs-N bond

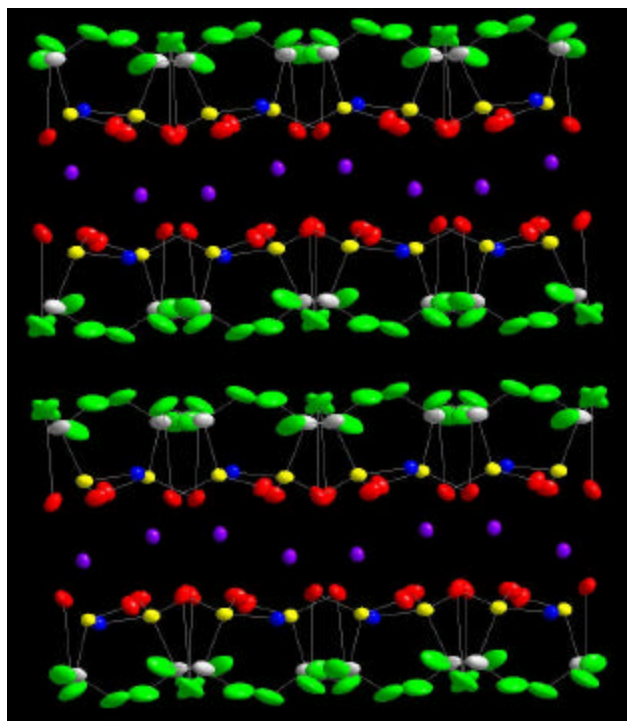




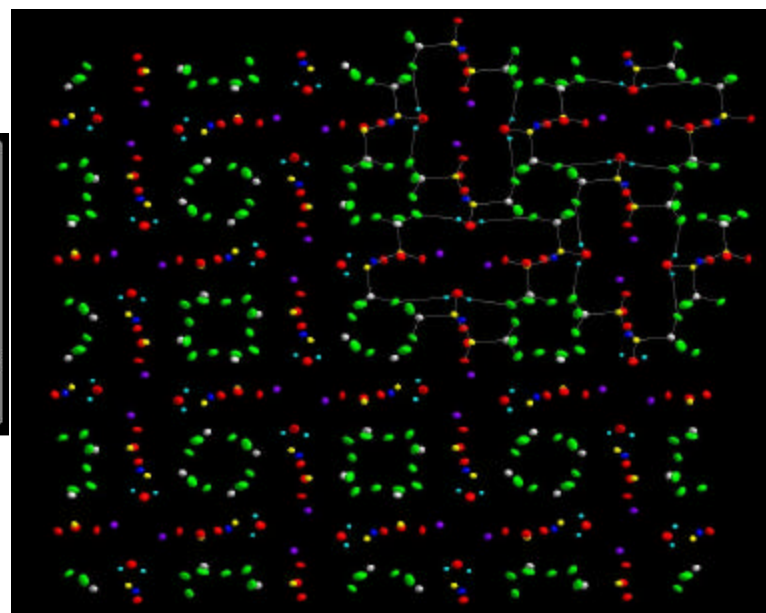
Crystal packing in $\text{CsN}(\text{SO}_2\text{CF}_3)_2$ salts



Hydrophobic and hydrophilic Layering

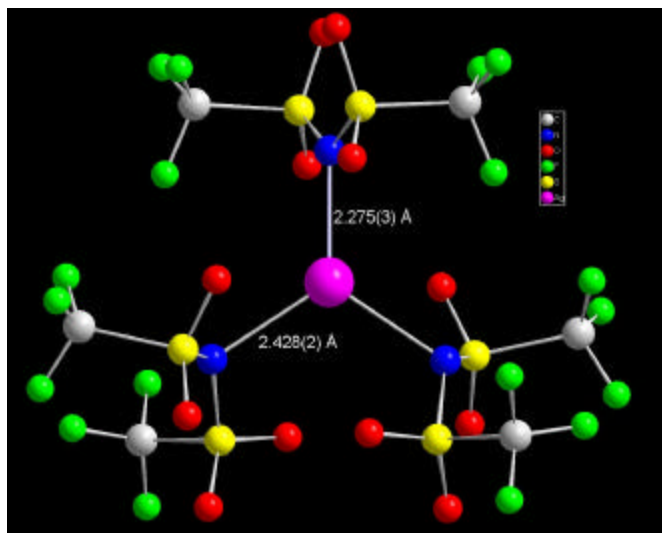


“Swiss cheese” Tunnel/channel structure





Polymorphism in $\text{AgN}(\text{SO}_2\text{CF}_3)_2$



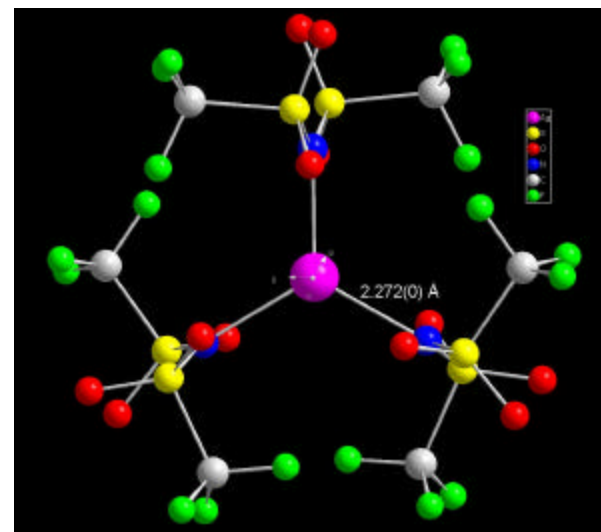
Unit cell dimensions (Å)

Orthorhombic $P2_1/n$

$a = 7.510(6)$, $b = 15.729(12)$, $c = 8.119(7)$

Volume (Å³) = 876.7(12), $Z = 4$, $T = 298\text{ K}$

$R1 = 0.1028$, $S = 1.84$



Unit cell dimensions (Å)

Trigonal $P-3_1c$

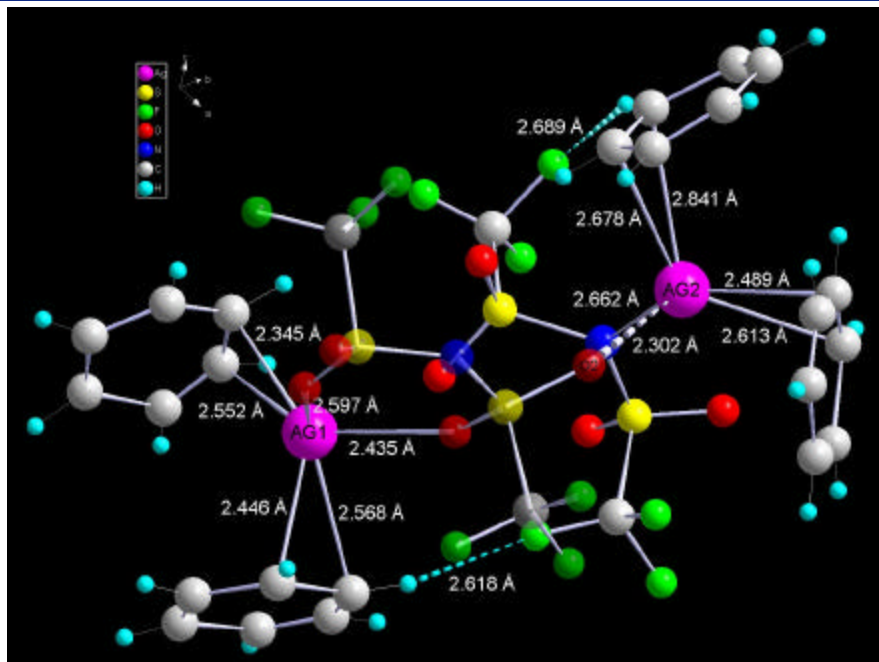
$a = 7.510(6)$, $c = 8.119(7)$

Volume (Å³) = 876.7(12), $Z = 6$, $T = 298\text{ K}$

$R1 = 0.1028$, $S = 1.84$



Structure of $[AgN(SO_2CF_3)_2(C_6H_6)_2]$



- ✓ Dimerization via S-O...Ag bonding (2.302 Å)
- ✓ Long unsymmetrical Ag-C bonds
- ✓ $N(SO_2CF_3)_2$ group is “transoid”
- ✓ H...F bond distances observed close to sum of van der Waal distance

Triclinic $P-1$

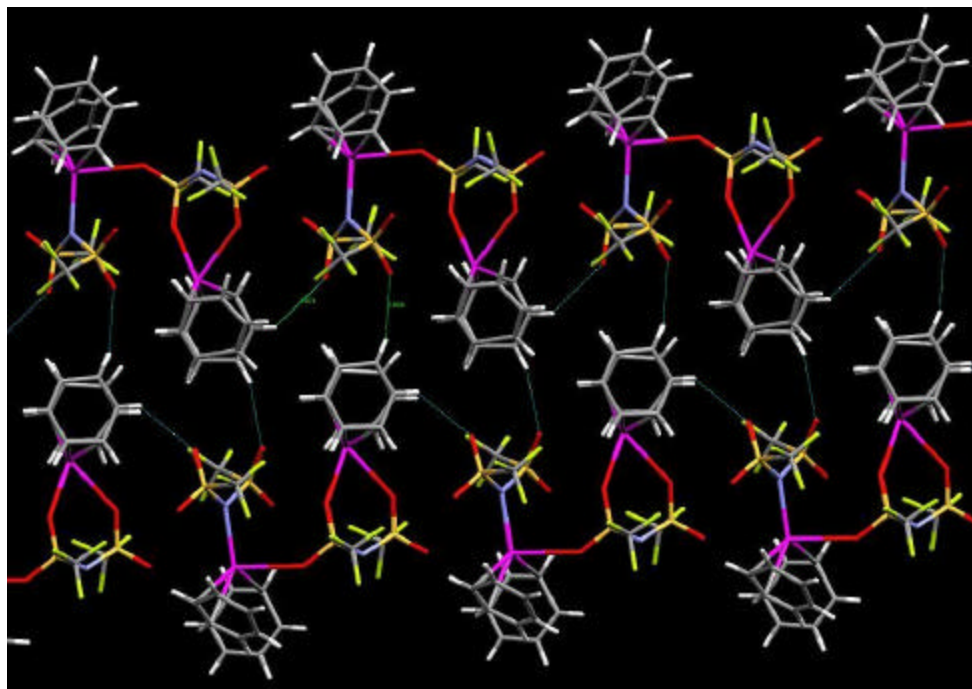
$a = 7.6704(13) \text{ \AA}$, $b = 8.4295(14) \text{ \AA}$, $c = 8.8631(15) \text{ \AA}$,

$\alpha = 111.673(3)^\circ$, $\beta = 108.479(3)^\circ$, $\gamma = 97.798(3)^\circ$

$V (\text{ \AA}^3) = 483.89(14)$, $Z = 2$, $T = 298(2) \text{ K}$; $R1 = 0.0432$, $S = 1.114$

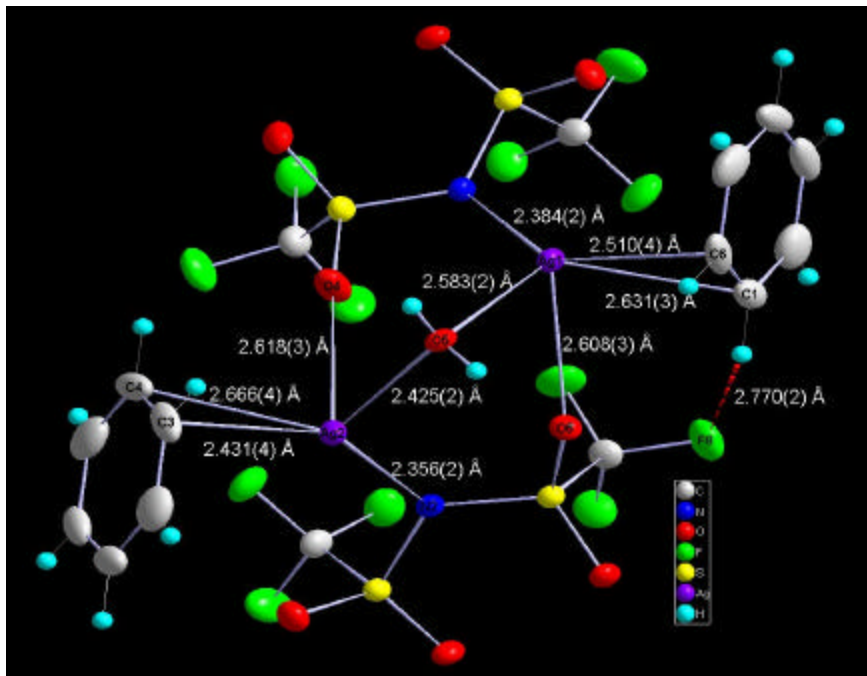


Crystal packing in $[AgN(SO_2CF_3)_2(C_6H_6)_2]$





Structure of $[AgN(SO_2CF_3)_2(C_6H_6)]_2 \cdot H_2O$



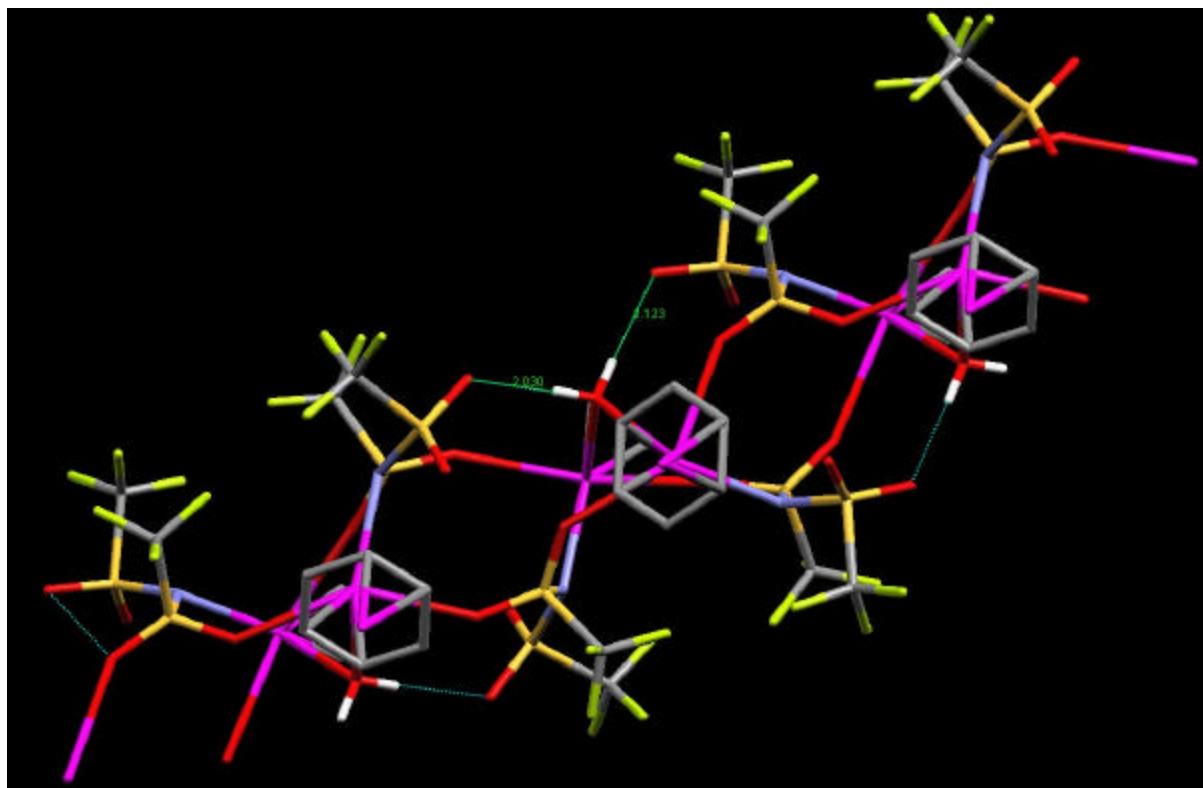
Monoclinic $P2_1/n$

$a = 10.372(1) \text{ \AA}$, $b = 19.823(2) \text{ \AA}$, $c = 12.406(1) \text{ \AA}$, $\beta = 108.536(3)^\circ$,
 $V (\text{ \AA}^3) = 2148.5(5)$, $Z = 8$, $T = 173(1) \text{ K}$; $R1 = 0.0224$, $S = 1.04$

- ✓ $N(SO_2CF_3)_2$ group is both N- as well as O-bonded to silver
- ✓ Water bridges the eighth-membered Ag-O-S-N-Ag-O-S-N ring forming two fused six-membered rings.
- ✓ Unsymmetrical Ag-C bonds
- ✓ $N(SO_2CF_3)_2$ group is “cisoid”
- ✓ H...F bond distances observed close to sum of van der Waal distance



Crystal packing in $[AgN(SO_2CF_3)_2(C_6H_6)]_2 \cdot H_2O$



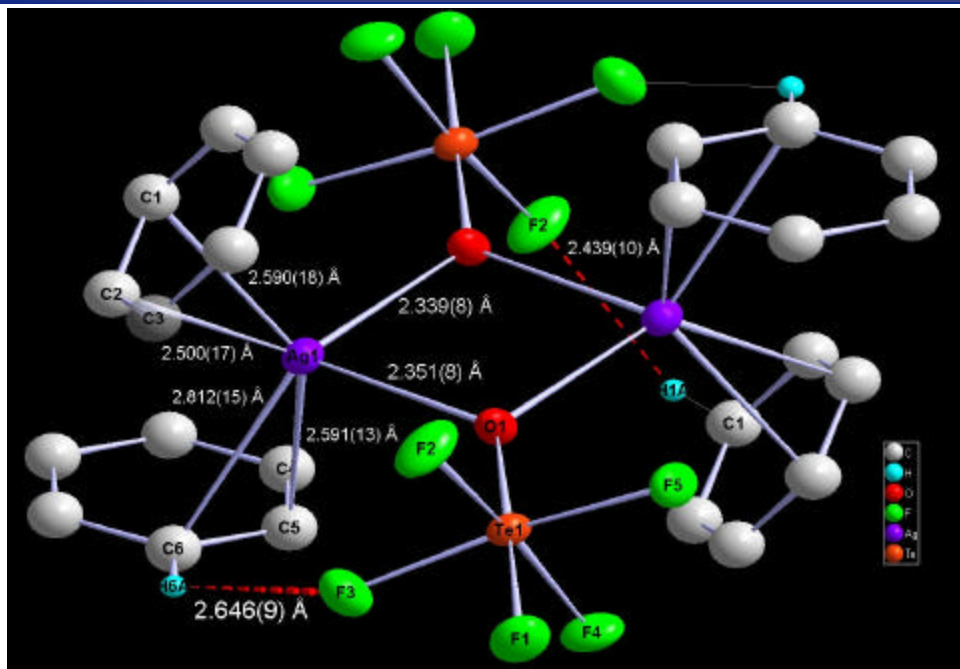
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Structure of $[AgOTeF_5(C_6H_6)_2]_2$



- ✓ Dimeric structure
- ✓ Unsymmetrical Ag-C bonds
- ✓ Unsymmetrical and very long Te-O bonds
- ✓ H...F bonds observed

Triclinic $P-1$

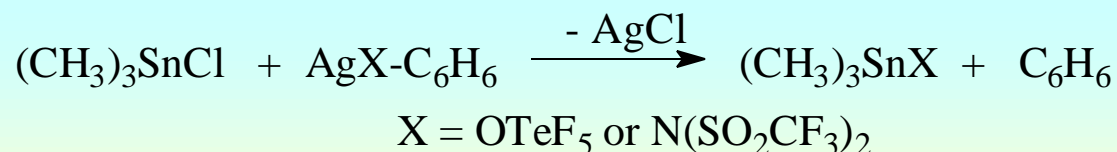
$a = 7.6704(13) \text{ \AA}$, $b = 8.4295(14) \text{ \AA}$, $c = 8.8631(15) \text{ \AA}$,

$\alpha = 111.673(3)^\circ$, $\beta = 108.479(3)^\circ$, $\gamma = 97.798(3)^\circ$

$V (\text{ \AA}^3) = 483.89(14)$, $Z = 2$, $T = 298(2) \text{ K}$; $R1 = 0.0432$, $S = 1.114$



Reaction of silver salts: Synthesis of trimethyltin(IV) derivatives



MS shows [M-CH₃]⁺ peak

Trimethyltin(IV) teflate can be distilled at 50 °C under vacuum (0.1 T)

nTe-O (cm⁻¹): IR (Ra) at 860 (856)

nSn-C (cm⁻¹) IR (Ra): asym: 552 (554); sym 518 (518)

n_{as}SO₂ (cm⁻¹): IR (Ra) at 1342(1327)

nSn-C (cm⁻¹) IR (Ra): asym: 558 (556); sym 520 (513)

nTe-O (cm⁻¹) F₅TeOCl: IR (Ra) at 551 (554); nTe-O (cm⁻¹) F₅TeOTBA: IR (Ra) at 867 (866);

- ✓ Trimethyltin(IV) derivatives are colorless viscous oils.
- ✓ Highly moisture sensitive
- ✓ Potentially stronger catalysts in organic synthesis compared to TMSOTf



What is so interesting about $(\text{CH}_3)_3\text{Sn}$ derivatives of strong acids??



- ✓ **The Sn-C bond cleavage can be selective i.e., there is a competition between Sn-C and Sn-Cl bond cleavage depending upon the acid used.**
 - ✓ **The trimethyltin(IV) derivatives of strong acids are extremely electrophilic reagents that have application in organic synthetic reactions.**
-
- ✓ **The electrophilic nature of an organotin(IV) compound can be reflected by its ^{119}Sn chemical shift i.e, deshielding. ^{119}Sn has a spin of $\frac{1}{2}$, relative abundance of 8.58 % and has high relative sensitivity (30x ^{13}C).**
 - ✓ **Can ^{119}Sn chemical shifts (in neat liquids or as a solution in “low-coordinating” solvents) be correlated to anion basicities in case of trimethyltin(IV) derivatives?**



Correlating spectroscopy and crystallography



Correlation of $^2J(^{119}\text{Sn}-^1\text{H})$ and C-Sn-C angle (determined from x-ray crystallography gives the following non-linear relationship:

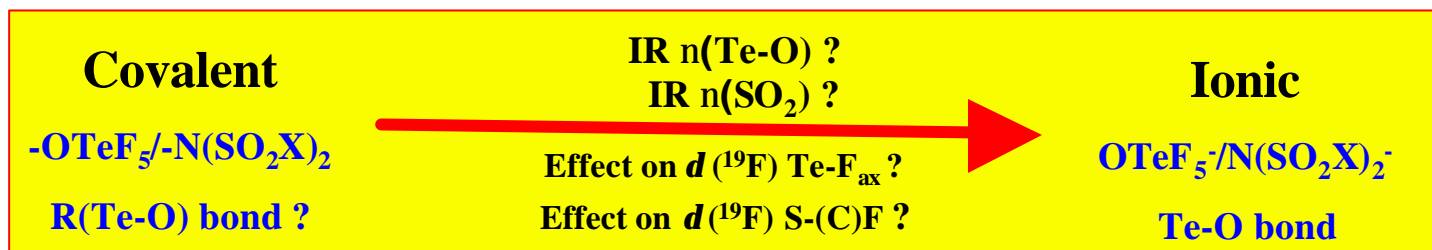
$$T(\text{C-Sn-C})^\circ = 0.0161 |^2J(^{119}\text{Sn}-^1\text{H})|^2 - 1.32 |^2J(^{119}\text{Sn}-^1\text{H})| + 133.4$$

Correlation of $^1J(^{119}\text{Sn}-^{13}\text{C})$ and C-Sn-C angle (determined from x-ray crystallography gives the following linear relation:

$$11.4T - 875 = |^1J(^{119}\text{Sn}-^{13}\text{C})|$$

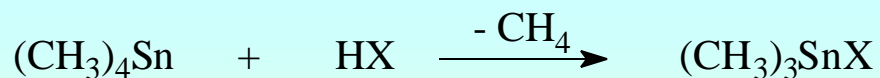
Lockhart, T. P.; Manders, W. F. *Inorg. Chem.* 1985, 25, 892

Lockhart, T. P.; Manders, W. F.; Zuckerman, J. J. *J. Am. Chem. Soc.* 1985, 107, 4546





Synthesis of trimethyltin(IV) derivatives



$\text{X} = \text{OTeF}_5 \text{ or } \text{N}(\text{SO}_2\text{CF}_3)_2$

MS shows $[\text{M}-\text{CH}_3]^+$ peak

Trimethyltin(IV) teflate can be distilled at 50 °C under vacuum (0.1 T)

$n\text{Te-O (cm}^{-1}\text{): IR (Ra) at 860 (856)}$

$n\text{Sn-C (cm}^{-1}\text{) IR (Ra): asym: 552 (554); sym 518 (518)}$

$n_{\text{as}}\text{SO}_2 \text{ (cm}^{-1}\text{): IR (Ra) at 1342(1327)}$

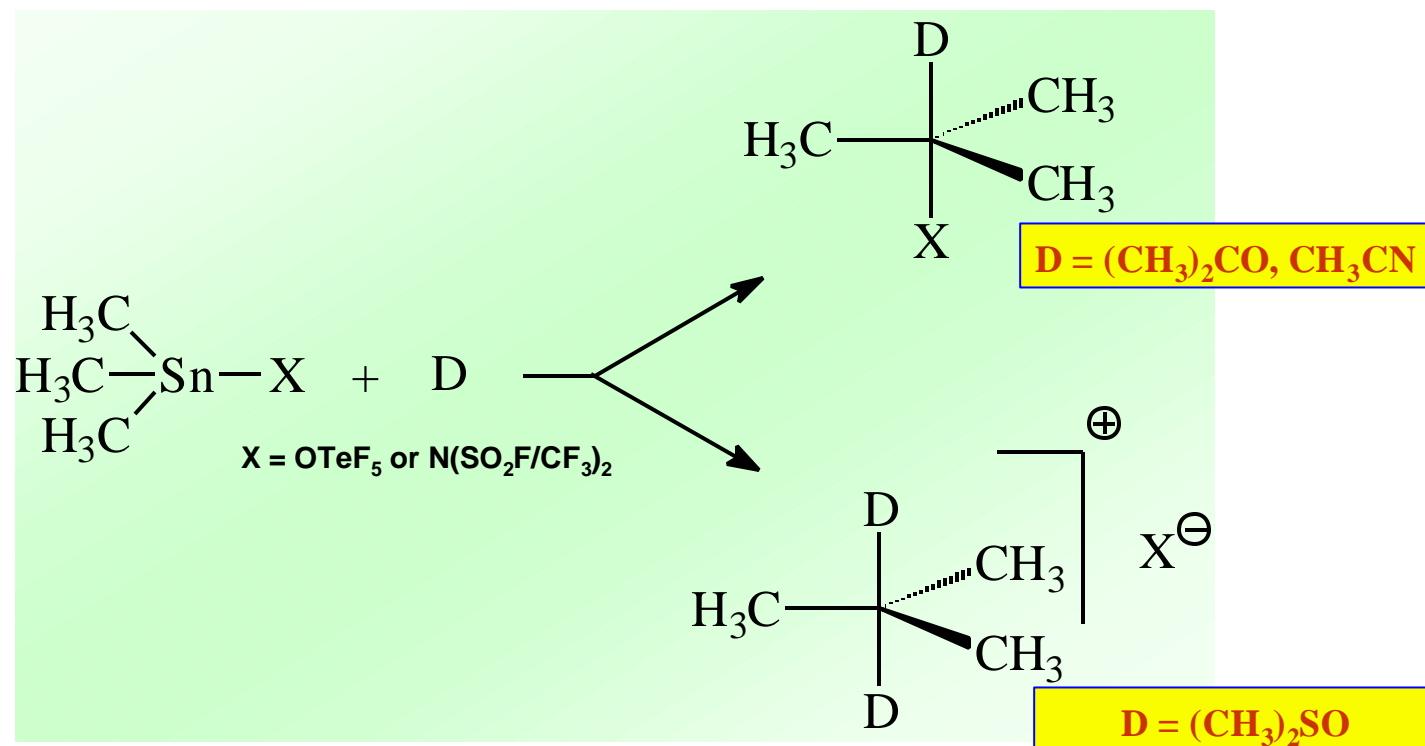
$n\text{Sn-C (cm}^{-1}\text{) IR (Ra): asym: 558 (556); sym 520 (513)}$

$n\text{Te-O (cm}^{-1}\text{) F}_5\text{TeOCl: IR (Ra) at 551 (554); } n\text{Te-O (cm}^{-1}\text{) F}_5\text{TeOTBA: IR (Ra) at 867 (866);$

- ✓ Tetramethyltin is used in large excess
- ✓ Reaction by-products can be easily removed under vacuum
- ✓ Trialkyltin(IV) derivatives are colorless viscous oils that are highly sensitive to moisture and donor solvents.

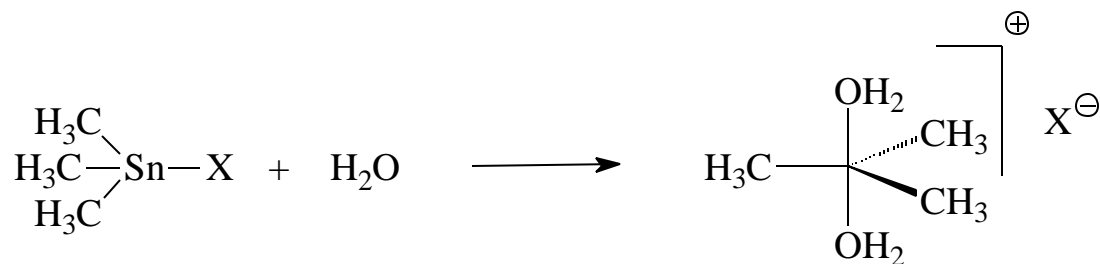


Coordination complex formation with donor solvents

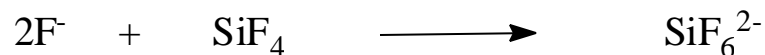
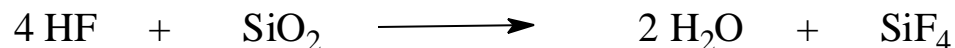
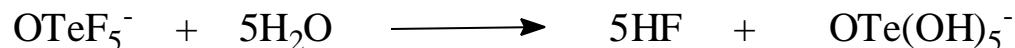




Formation of the hydrated trimethylstannyl cation



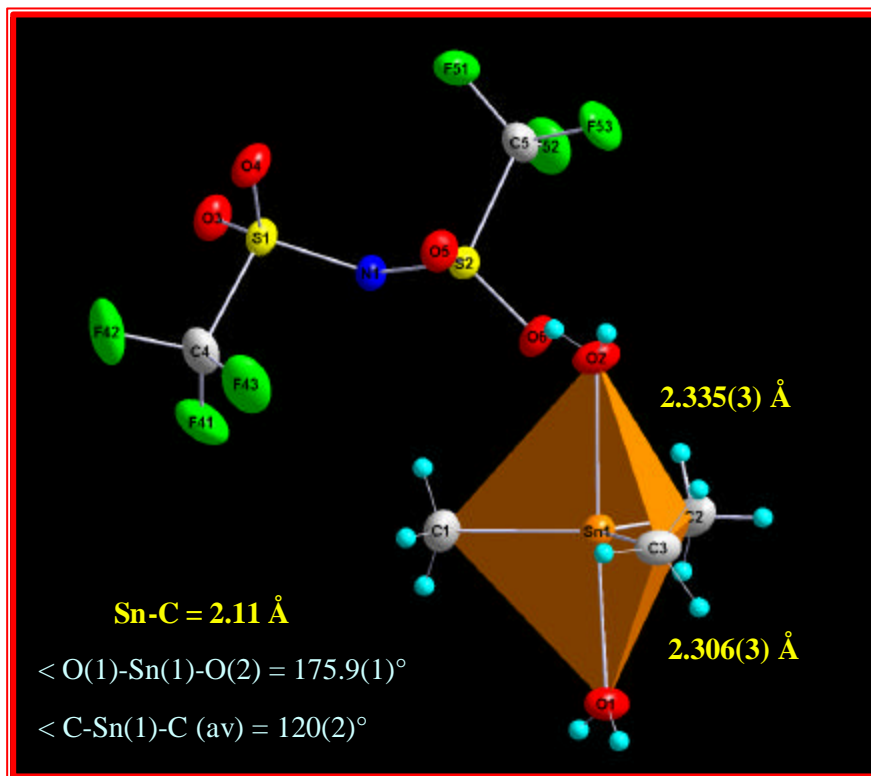
The hydrated salt can be isolated with $\text{N}(\text{SO}_2\text{CF}_3)_2$ anion but **NOT** for OTeF_5 anion.
The compound isolated after hydrolysis is $[\text{Me}_3\text{Sn}(\text{OH}_2)_2]_2\text{SiF}_6$



The hydrolysis of trimethyltin teflate results in the decomposition of the OTeF_5 group



Hydrated trimethyltin(IV) cation



Unit cell dimensions (Å)

Monoclinic ($P2_1/c$)

$a = 7.3072(1)$, $b = 13.4649(2)$,

$c = 16.821(2)$

$\beta = 98.705(1)^\circ$

Volume (Å³) = 1636.0(3) ,

$Z = 4$

$T = 213(2)$

$R1 = 0.0367$

$wR2 = 0.0736$

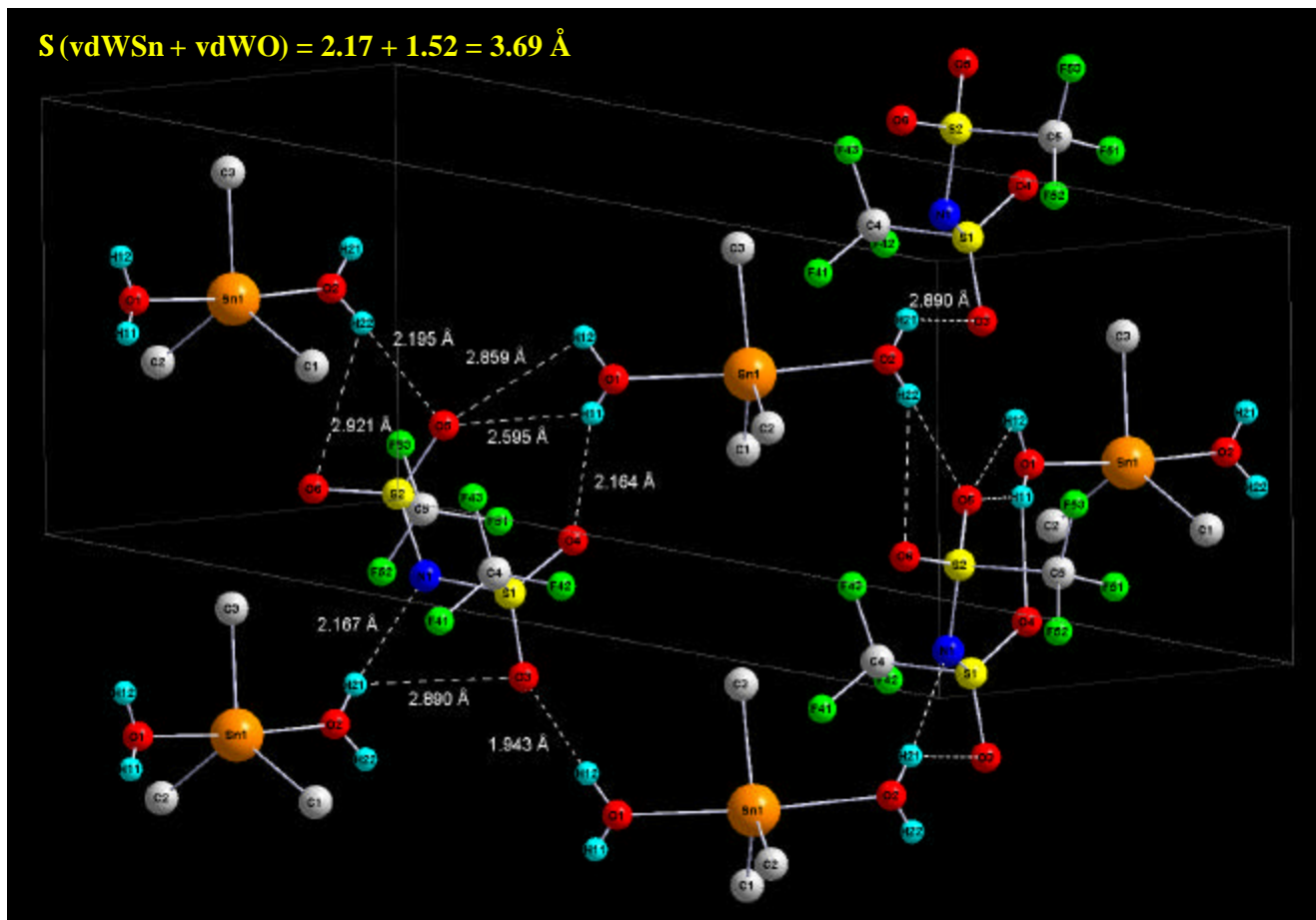
$S = 1.233$



Hydrogen bonding in hydrated trimethyltin(IV) cations



$$S(\text{vdWSn} + \text{vdWO}) = 2.17 + 1.52 = 3.69 \text{ \AA}$$



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Multinuclear NMR Parameters

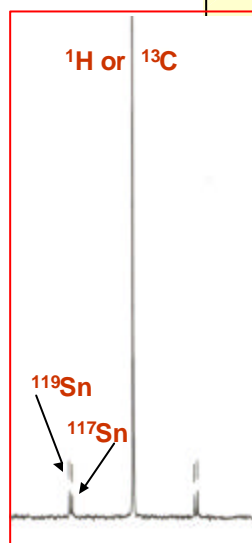


Table 1. ^1H , ^{13}C NMR Spectroscopic Data^a and calculated^{b,c} C-Sn-C angles for $(\text{CH}_3)_3\text{SnX}$ [X = OTeF_5 and $\text{N}(\text{SO}_2\text{F}/\text{CF}_3)_2$]

| Solute | Solvent ^d | $\delta(^1\text{H})$ ppm | $^2J(^{119}(\text{Sn})-^1\text{H})$ Hz | $\theta(\text{C-Sn-C})^b$ ($^\circ$) | $\delta(^{13}\text{C})$ ppm | $^1J(^{119}(\text{Sn})-^{13}\text{C})$ Hz | $\theta(\text{C-Sn-C})^c$ ($^\circ$) |
|--|----------------------------|-----------------------------|---|---|--------------------------------|--|---|
| $(\text{CH}_3)_3\text{SnOTeF}_5$ | neat | 0.84 | 59.2 ^e | 111.7 | 0.84 | 376.9(360.3) | 109.8 |
| | CH_2Cl_2 | 0.79 | 58.5(55.9) | 111.3 | 0.90 | 374.0(357.4) | 109.6 |
| | acetone | 0.69 | 68.8(65.8) | 118.8 | 1.55 | 480.4(459.3) | 118.9 |
| | CH_3CN | 0.66 | 69.2(66.2) | 119.2 | 1.49 | 484.6(463.1) | 119.3 |
| | DMSO | 0.50 | 69.5(66.6) | 119.4 | 1.05 | 511.4(490.0) | 121.6 |
| $(\text{CH}_3)_3\text{SnOTeF}_5$ | AN/ H_2O | 0.46 | 69.6(66.7) | 119.5 | 0.10 | 508.5(486.0) | 121.4 |
| | DMSO/ H_2O | 0.43 | 70.1(68.5) ^e | 120.0 | 0.84 | 515.5(492.5) | 122.0 |
| $(\text{CH}_3)_3\text{SnN}(\text{SO}_2\text{F})_2$ | neat | 0.91 | 63.8(61.6) | 114.7 | 1.6 | 416.8(400.3) | 113.3 |
| | CH_2Cl_2 | 0.96 | 62.3(59.9) | 113.6 | 1.4 | 404.1(387.7) | 112.2 |
| $(\text{CH}_3)_3\text{SnN}(\text{SO}_2\text{CF}_3)_2$ | DMSO | 0.83 | 72.4(70.0) | 122.2 | -0.2 | 528.3(509.9) | 123.1 |
| | neat | 0.84 | 64.2(61.6) | 115.0 | 2.1 | 412.6(394.1) | 113.0 |
| | CH_2Cl_2 | 0.81 | 64.4(61.8) | 115.2 | 0.8 | 414.8(395.2) | 113.0 |
| | CH_3CN | 0.82 | 70.2(67.1) | 120.1 | -1.7 | 489.5(467.6) | 119.7 |
| | DMSO | 0.48 | 69.0(67.4) | 119.0 | 0.7 | 512.2(499.0) | 121.6 |
| $[(\text{CH}_3)_3\text{Sn}(\text{H}_2\text{O})_2][\text{N}(\text{SO}_2\text{CF}_3)_2]$ | CH_3CN | 0.61 | 69.7(66.7) | 119.6 | 0.10 | 491.8(470.0) | 120.0 |
| | DMSO | 1.18 | 69.8(66.7) | 119.7 | 0.92 | 512.9(497.2) | 121.8 |

^a NMR spectroscopic data were recorded at 300 K.

^b Calc from relation: $\theta = 0.0161 [^2J(^{119}\text{Sn}-^1\text{H})]^2 - 1.32 [^2J(^{119}\text{Sn}-^1\text{H})] + 133.4$.

^c Calc from relation: $[^1J(^{119}\text{Sn}-^{13}\text{C})] = 11.4 \theta - 875$.

^d Acetone = $(\text{CD}_3)_2\text{CO}$, DMSO = $(\text{CD}_3)_2\text{SO}$.

^e Calculated from center of unresolved ^{119}Sn , ^{117}Sn satellites ($|J_{\text{obs}}| \times 1.023$)



Multinuclear NMR parameters ...continued



Table 2. ^{19}F , ^{119}Sn and ^{125}Te NMR Spectroscopic Data^a of $(\text{CH}_3)_3\text{SnX}$ [$\text{X} = \text{OTeF}_5$ and $\text{N}(\text{SO}_2\text{F}/\text{CF}_3)_2$]

| Solute | Solvent ^b | $\delta(^{19}\text{F})$, ppm | | | $^2J(^{19}\text{F}_{\text{ax}}-^{19}\text{F}_{\text{eq}})$ Hz | $\delta(^{119}\text{Sn})$ ppm | $\delta(^{125}\text{Te})$ ppm | $\delta(^{13}\text{CF}_3)$ ppm | $^1J(^{125}\text{Te}-^{19}\text{F})$, Hz | | |
|--|--------------------------|-------------------------------|------------------------|-----------------------------------|--|----------------------------------|----------------------------------|-----------------------------------|---|------------------------|-------|
| | | F_{ax} | F_{eq} | $\text{CF}_2/\text{SO}_2\text{F}$ | | | | | F_{ax} | F_{eq} | Hz |
| $(\text{CH}_3)_3\text{SnOTeF}_5$ | neat | -32.9 | -41.9 | | 182.5 | 270.8 ^c | 569.5 | | 3112 | 3540 | |
| | CH_2Cl_2 | -30.3 | -38.5 | | 183.0 | 272.4 | 564.6 | | 3188 | 3550 | |
| | acetone | -29.1 | -40.6 | | 180.0 | 96.0 | 574.9 | | 3020 | 3558 | |
| | CH_3CN | -29.2 | -40.8 | | 179.0 | 84.2 | 575.0 | | 3032 | 3556 | |
| | DMSO | -16.2 | -33.8 | | 170.0 | 40.0 | 598.7 | | 2712 | 3666 | |
| $(\text{CH}_3)_3\text{SnN}(\text{SO}_2\text{F})_2$ | neat | | | 55.5 | 242.5 | | | | | | |
| | CH_2Cl_2 | | | 55.6 | 248.6 | | | | | | |
| | DMSO | | | 52.5 | 32.9 | | | | | | |
| $(\text{CH}_3)_3\text{SnN}(\text{SO}_2\text{CF}_3)_2$ | neat | | | -78.5 | 240.2 | | 118.7 | | | | 320.4 |
| | CH_2Cl_2 | | | -78.8 | 251.0 | | 118.1 | | | | 319.8 |
| | CH_3CN | | | -78.9 | 44.9 | | 119.4 | | | | 320.7 |
| | DMSO | | | -78.6 | 37.4 | | 120.0 | | | | 321.7 |
| $[(\text{CH}_3)_3\text{Sn}(\text{H}_2\text{O})_2][\text{N}(\text{SO}_2\text{CF}_3)_2]$ | CH_3CN | | | -79.0 | 59.0 | | | | | | |
| | DMSO | | | -79.1 | 42.8 | | | | | | |

^a NMR spectroscopic data were recorded at 300 K

^b Acetone = $(\text{CD}_3)_2\text{CO}$, DMSO = $(\text{CD}_3)_2\text{SO}$

^c ^{119}Sn NMR shows a peak at 300.7 ppm in HOTeF_5

$^{19}\text{F}_{\text{ax}}$ NMR for TEAOTeF_5 = -25.4 ppm

$\text{B}(\text{OTeF}_5)_3$ = -46.2 (Strauss et al., 1986)



^{119}Sn chemical shifts and anion basicity



- $d(^{119}\text{Sn})$ values lower (more downfield) than +200 ppm show a highly deshielded tin nuclei. Sometimes stronger acids results in relatively higher (upfield) chemical shifts due to close contacts even in solution state:

| <u>Compound (Me_3SnX)</u> | <u>$d(^{119}\text{Sn})$</u> |
|--|--|
| $\text{X} = \text{ClO}_4$ (unidentate) | 245 |
| $\text{X} = \text{SO}_3\text{CF}_3$ (bidentate) | 162 |

For trimethyltin(IV) derivatives in dichloromethane solution the relative anion basicity can be ordered as:

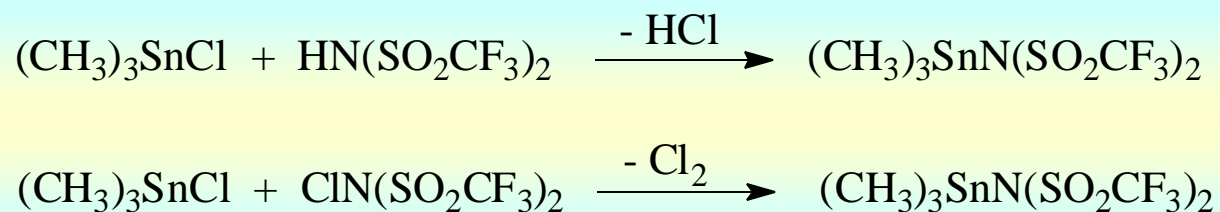




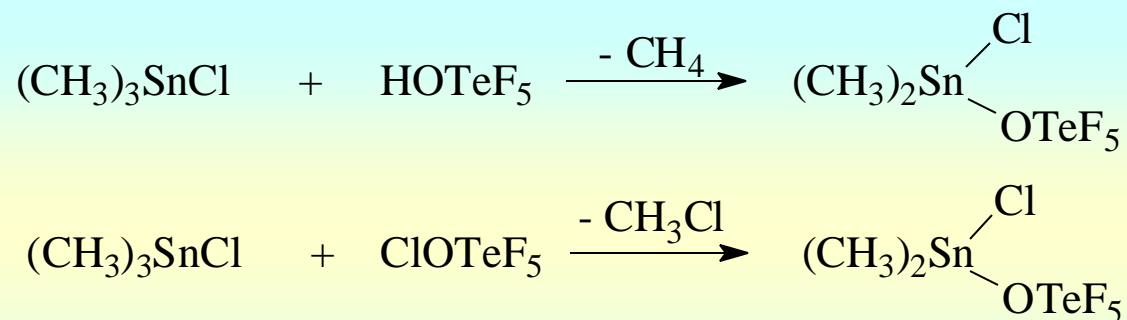
Sn-C versus Sn-Cl bond cleavage



$\text{XN}(\text{SO}_2\text{CF}_3)_2$ (X = H, Cl) shows a preferential Sn-Cl bond cleavage



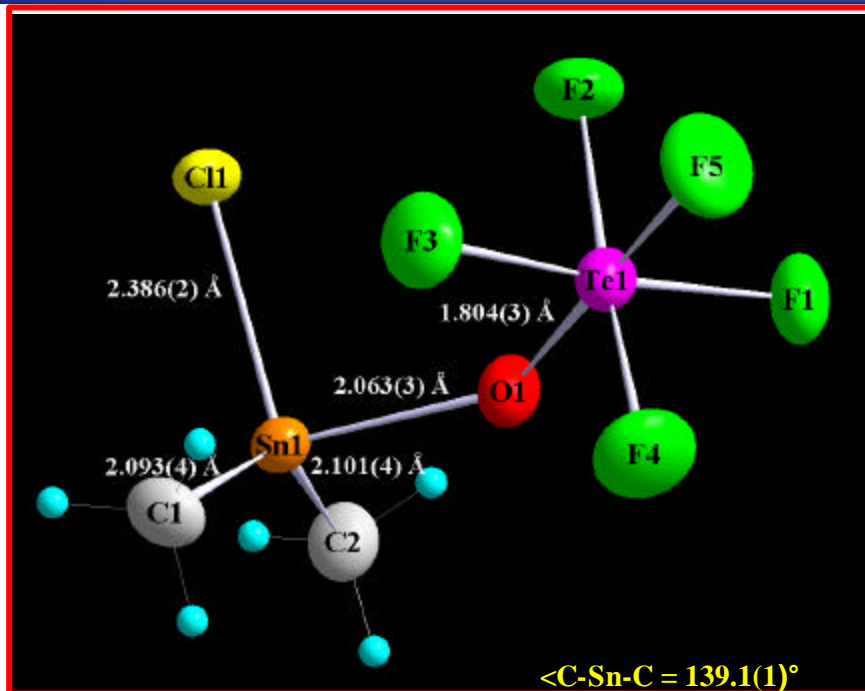
XOTeF_5 (X = H, Cl) shows a preferential Sn-C bond cleavage



According to Sladky and Kropshofer (*JCS Chem. Commun.*, 1973, 600), reaction of $(\text{CH}_3)_3\text{SnCl}$ with HOTeF_5 gives trimethyltin(IV) teflate exclusively!



Structure of $(\text{CH}_3)_2\text{Sn}(\text{Cl})\text{OTeF}_5$



Unit cell dimensions (\AA)

Monoclinic $P2_1/n$

$a = 5.8204(8)$, $b = 10.782(1)$,

$c = 15.493(2)$

$\beta = 99.59(1)^\circ$

Volume (\AA^3) = 971.7(2)

$Z = 4$

$T = 218(2) \text{ K}$

$R1 = 0.0282$

$wR2 = 0.0712$

$S = 1.088$

$\text{Te}-\text{O} (\text{\AA}) (\text{X}=\text{OTeF}_5) : \text{B}(\text{X})_3 = 1.874(6)$; $[\text{TBA}][\text{H}(\text{X})_2] = 1.800(4)\text{av}$; $[\text{Au}(\text{X}_3)]_2 = 1.91(2)$

Strauss et al., Inorg. Chem., 1986, 25, 2806 and references therein

$n(\text{TeO}) = 856 \text{ cm}^{-1}$ in IR and Ra; $n(\text{SnO}) = 427 (\text{IR})/424 (\text{Ra}) \text{ cm}^{-1}$; $n(\text{SnCl}) = 313 (\text{Ra}) \text{ cm}^{-1}$



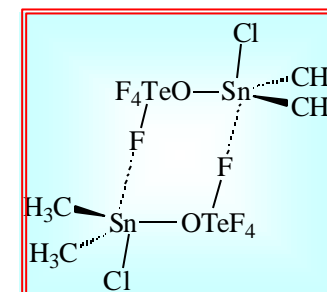
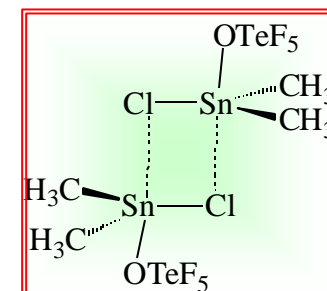
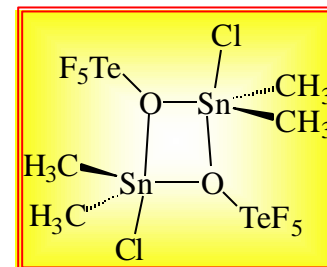
Tetra- or pentacoordinated tin???



The C-Sn-C angle calculated using $^2J(^{119}\text{Sn}-^1\text{H})$ (67.9 Hz) and $^1J(^{119}\text{Sn}-^{13}\text{C})$ (472 Hz) coupling constants for $(\text{CH}_3)_2\text{SnCl}(\text{OTeF}_5)$ dissolved in CD_2Cl_2 is approximately $\sim 118^\circ$. The $d(^{119}\text{Sn})$ value of ~ 142.7 ppm indicates that tin is present in a five-coordinate environment. The fifth coordination site can be occupied by a bridging chlorine, fluorine or oxygen from a neighboring $\text{Me}_2\text{SnCl}(\text{OTeF}_5)$ molecule.

^{119}Sn NMR show the presence of another broad peak at ~ 127 ppm, which is due to an equilibrium. In VT NMR studies using toluene- d_8 as a solvent, this peak disappears at -80°C .

Mass spectrum shows $[\text{M}-\text{CH}_3]^+$ peak as the highest peak indicating that the dimer is not stable in the gas phase

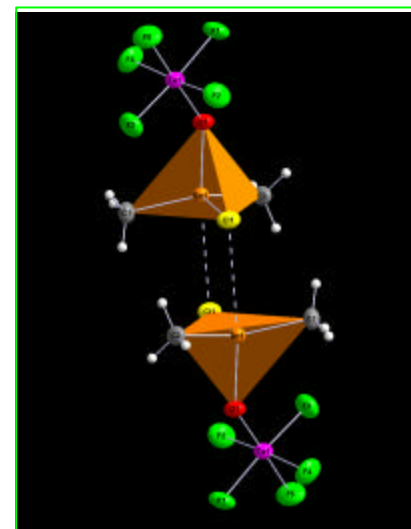
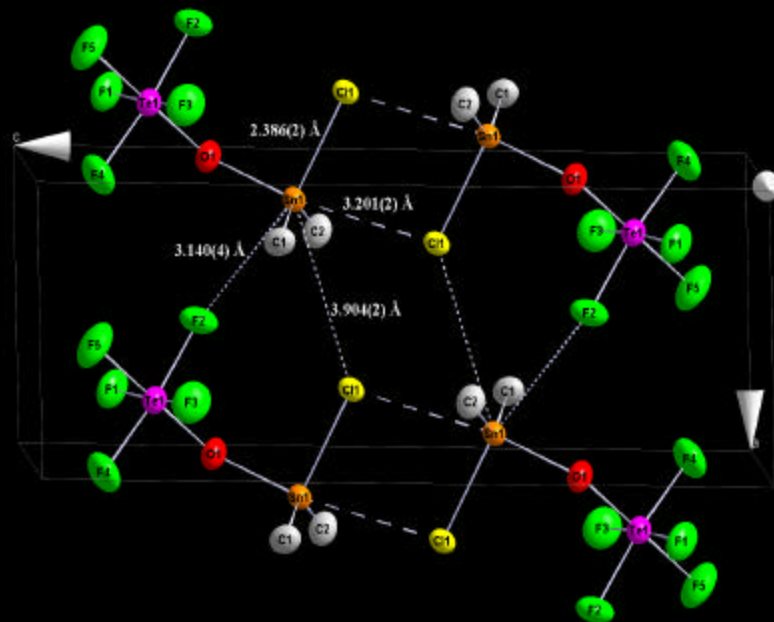




Coordination environment around tin



Sn-Cl contact found in the crystal lattice is 3.201(1) Å, which is much shorter than the sum of van der Waal radii of tin and chlorine. A longer Sn-Cl contact is also present at 3.904(2) Å.
 $S(\text{vdWSn} + \text{vdWCl}) = 2.17 + 1.75 = 3.92 \text{ Å}$

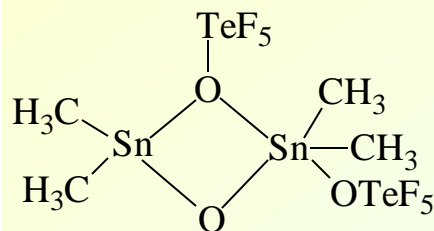
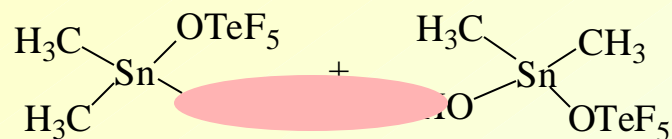
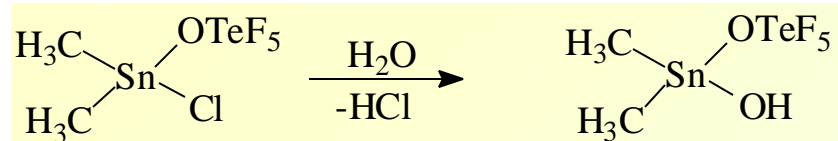


One Sn-F contact is also found in the crystal lattice 3.140(4) Å, which is much shorter than the sum of van der Waal radii of tin and fluorine.

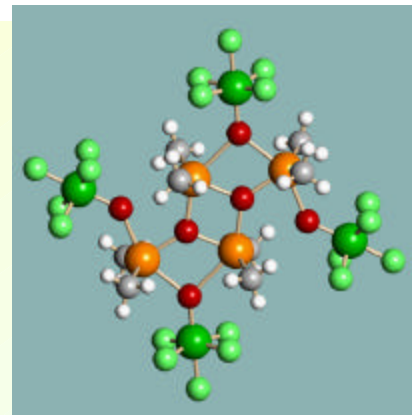
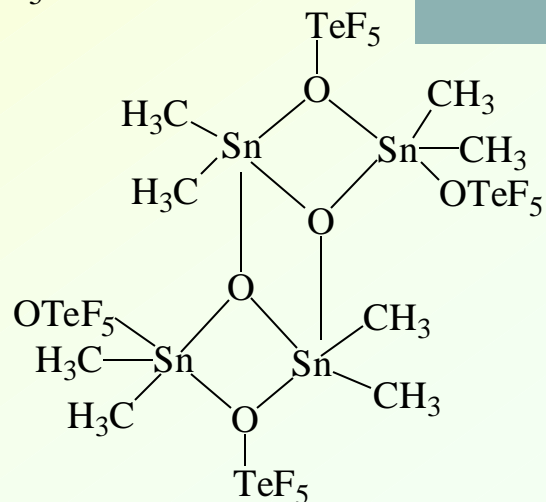
$$S(\text{vdWSn} + \text{vdWF}) = 2.17 + 1.47 = 3.64 \text{ Å}$$



Hydrolysis of the Sn-Cl bond in $(\text{CH}_3)_2\text{Sn}(\text{Cl})\text{OTeF}_5$

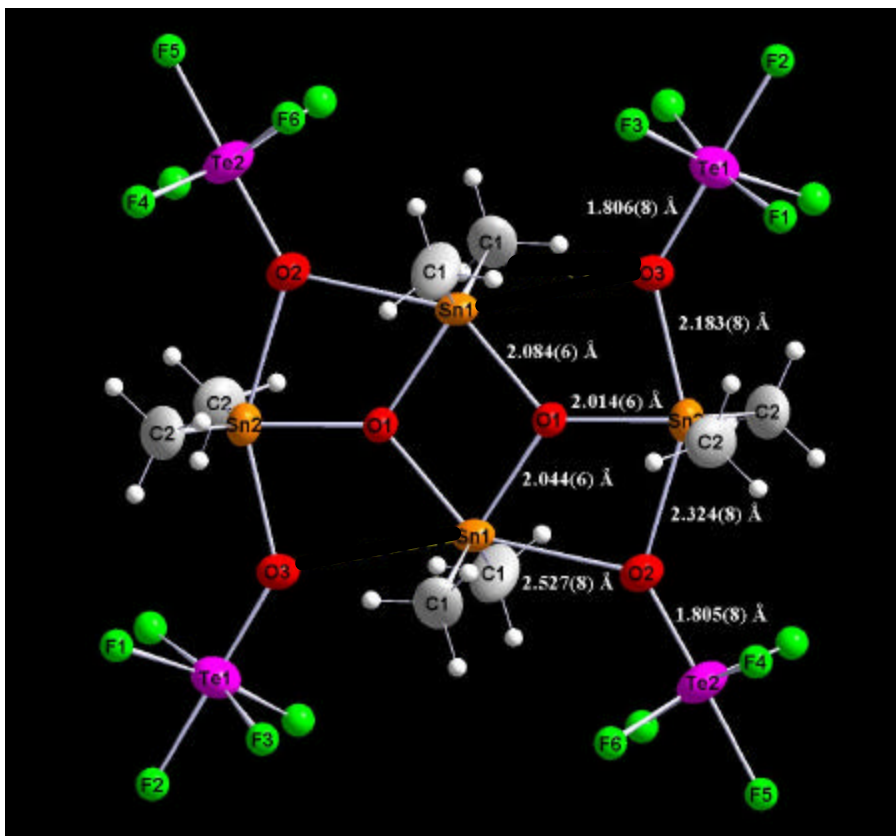


$\xrightarrow{\text{Dimerization}}$





Structure of the dimethyloxotin(IV) teflate



Unit cell dimensions (Å)

Orthorhombic

Space Group: *Pnnm*

$a = 12.574(6)$, $b = 12.667(6)$,

$c = 11.682(5)$

Volume (Å³) = 1860.6(1)

$Z = 2$

$T = 243\text{ K}$

$R1 = 0.0376$

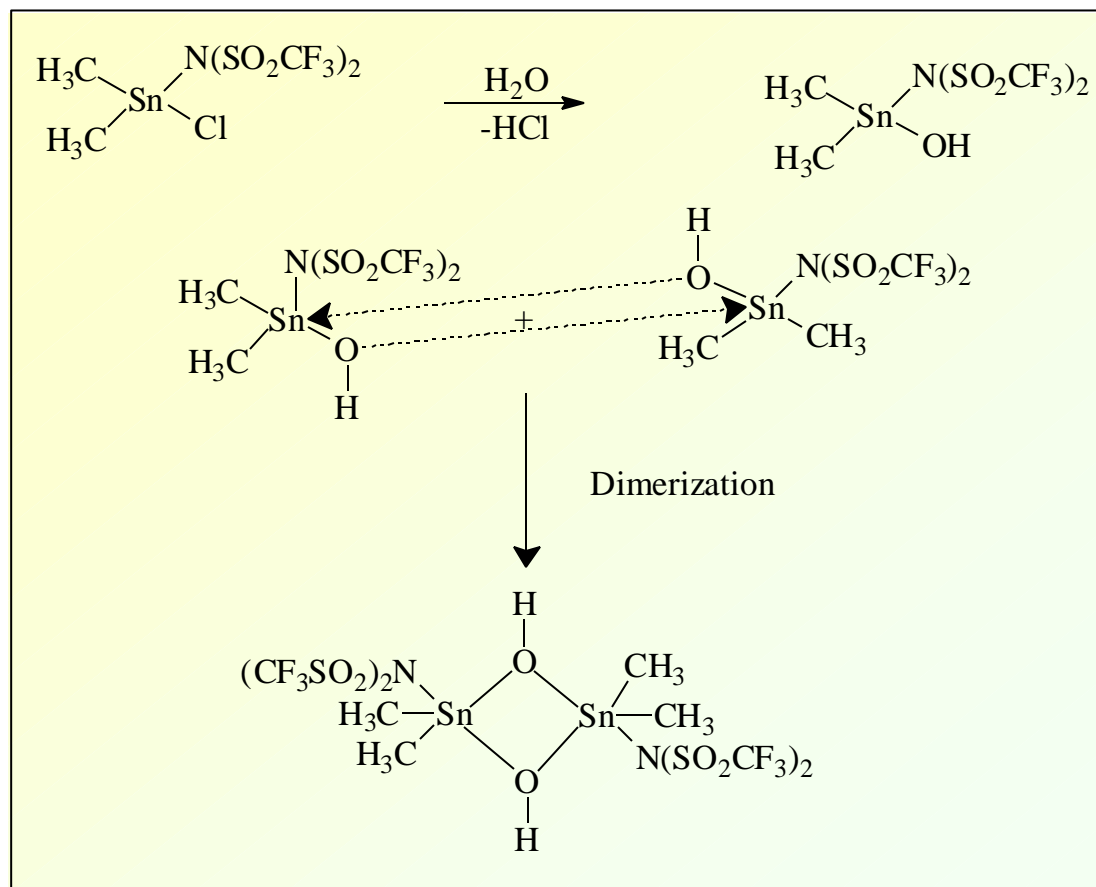
$wR2 = 0.1021$

$S = 1.04$

$S(\text{vdWSn} + \text{vdWO}) = 2.17 + 1.52$
 $= 3.69\text{ Å}$

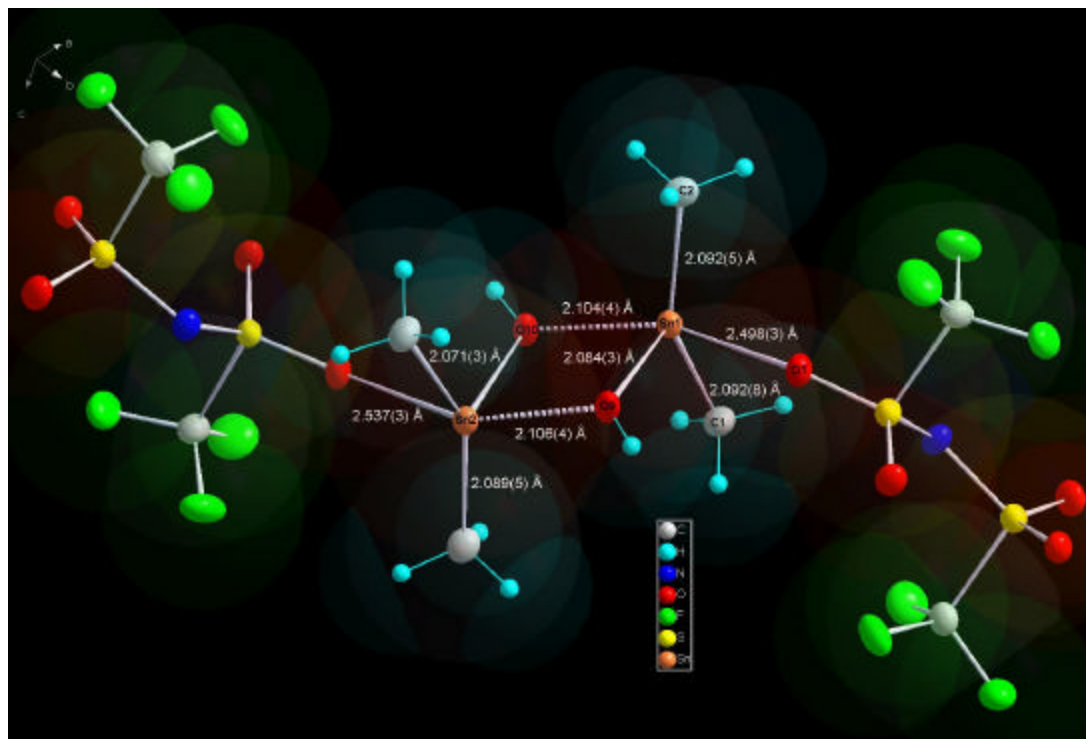


Hydrolysis of the Sn-Cl bond in $(\text{CH}_3)_2\text{Sn}(\text{Cl})\text{N}(\text{SO}_2\text{CF}_3)_2$





Structure of $\text{Me}_2\text{Sn}(\text{OH})\text{N}(\text{SO}_2\text{CF}_3)_2$

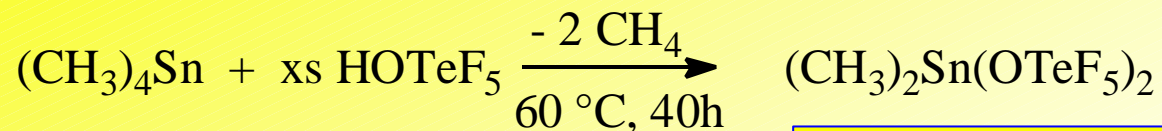




Solvolysis of Me_4Sn in excess acid: Synthesis of dimethyltin(IV) teflate

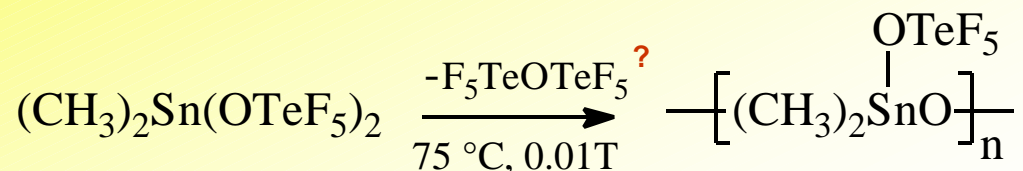


- ✓ **Dimethyltin(IV) teflate is formed when tetramethyltin is reacted with excess teflic acid**



MS shows $[\text{M}-\text{CH}_3]^+$ peak

- ✓ **Upon sublimation $\sim 75\text{ }^\circ\text{C}/0.01\text{T}$ a polymeric species is formed, probably due to the loss of $\text{O}(\text{TeF}_5)_2$**



$n(\text{TeO}) = 877\text{ cm}^{-1}$; $n(\text{SnO}) = 434\text{ (IR) cm}^{-1}$; $n_{\text{as}}(\text{SnC}) = 591\text{ cm}^{-1}$, $n_{\text{s}}(\text{SnC}) = 531\text{ cm}^{-1}$



Structure of dimethyltinooxteflate



Unit cell dimensions (\AA)

Monoclinic $P2_1/n$

Rotational TWIN

$a = 7.510(6)$, $b = 15.729(12)$,

$c = 8.119(7)$

$\beta = 115.1(1)^\circ$

Volume (\AA^3) = 876.7(12)

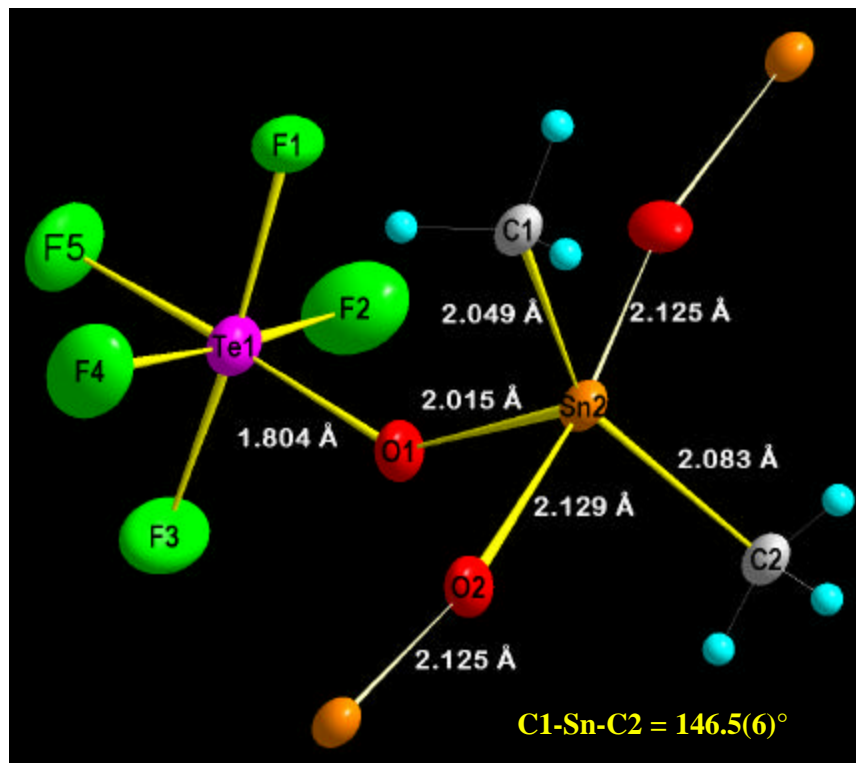
$Z = 4$

$T = 233(2) \text{ K}$

$R1 = 0.1028$

$S = 1.84$

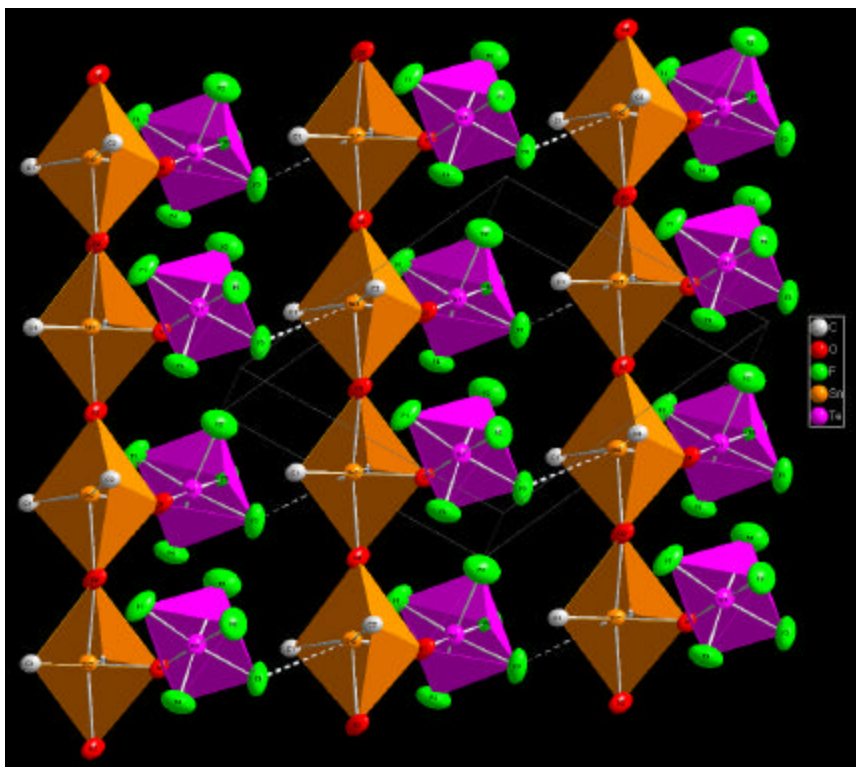
BASF = 0.256



$\text{C1-Sn-O1} = 110.2(5)^\circ$; $\text{C2-Sn-O1} = 103.3(6)^\circ$,
 $\langle \text{equi. X-Sn-X (av)} \rangle = 120^\circ$; $\text{O2-Sn-O2}^* = 169.9(5)^\circ$



Crystal packing showing tin and tellurium polyhedra



$$S_{(\text{vdwSn} + \text{vdwF})} = 2.17 + 1.47 \\ = 3.64 \text{ \AA}$$

$$\text{Sn-F distance in the crystal packing} \\ = 3.107(16) \text{ \AA}$$

The structure shows polymeric Sn-O chains bridged by a fluorine atom of the OTeF_5 group.

$$\angle \text{Sn-O2-Sn}^* = 167.2^\circ$$

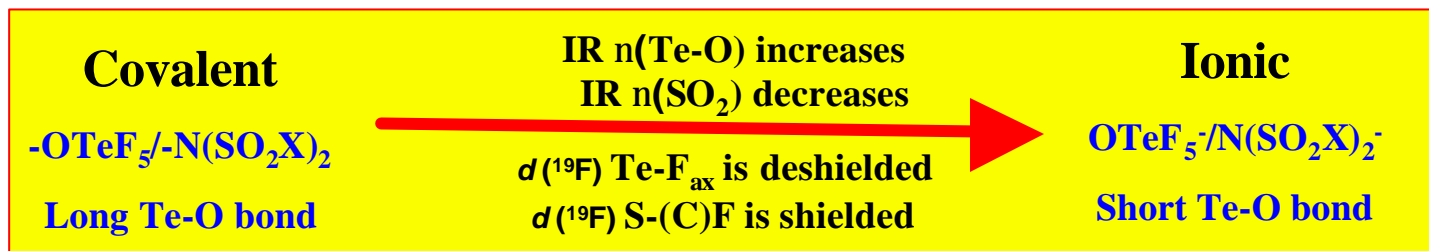
$$(\text{Sn}^* = \frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z)$$



Conclusions



- Trimethyltin(IV) teflates/F-imides are highly electrophilic in nature and form 1:1 or 1:2 complexes with donor solvents
- ^{119}Sn NMR chemical shifts can reflect the “electrophilic strength” and relative anion basicity for a Me_3Sn (IV) compound.
- During the solvolysis of trimethyltinchloride in HOTeF_5 , there is a preferential cleavage of the Sn-C bond versus Sn-Cl bond
- Chlorodimethyltin(IV) teflate hydrolyzes to form a Sn-O ladder compound and sublimation of dimethyltin(II) bis(teflate) results in the formation of an oxo-bridged species.





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ERC Inc.



BACKUP/SUPPL. SLIDES



BACKUP



Bond distances and angles $\text{Me}_2\text{SnClOTeF}_5$



| | | | |
|--------------|----------|-----------------|------------|
| • Sn(1)-C(2) | 2.104(4) | C(2)-Sn(1)-C(1) | 117.8(2) |
| • Sn(1)-C(1) | 2.115(4) | C(2)-Sn(1)-C(3) | 120.1(2) |
| • Sn(1)-C(3) | 2.120(4) | C(1)-Sn(1)-C(3) | 122.1(2) |
| • Sn(1)-O(1) | 2.306(3) | C(2)-Sn(1)-O(1) | 89.83(15) |
| • Sn(1)-O(2) | 2.335(3) | C(1)-Sn(1)-O(1) | 92.3(2) |
| • S(1)-O(3) | 1.427(2) | C(3)-Sn(1)-O(1) | 87.19(13) |
| • S(1)-O(4) | 1.428(3) | C(2)-Sn(1)-O(2) | 91.04(15) |
| • S(1)-N(1) | 1.573(3) | C(1)-Sn(1)-O(2) | 90.8(2) |
| • S(1)-C(4) | 1.825(5) | C(3)-Sn(1)-O(2) | 88.95(13) |
| • S(2)-O(6) | 1.421(3) | O(1)-Sn(1)-O(2) | 175.94(11) |
| • S(2)-O(5) | 1.433(3) | O(3)-S(1)-O(4) | 118.5(2) |
| • S(2)-N(1) | 1.589(3) | O(3)-S(1)-N(1) | 107.6(2) |
| • S(2)-C(5) | 1.844(4) | O(4)-S(1)-N(1) | 116.1(2) |
| | | O(3)-S(1)-C(4) | 104.0(2) |
| | | O(4)-S(1)-C(4) | 105.4(2) |
| | | O(6)-S(2)-O(5) | 118.2(2) |
| | | O(6)-S(2)-N(1) | 109.0(2) |
| | | O(5)-S(2)-N(1) | 115.3(2) |
| | | O(6)-S(2)-C(5) | 104.7(2) |
| | | O(5)-S(2)-C(5) | 105.0(2) |
| | | S(1)-N(1)-S(2) | 125.3(2) |